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Comprehensive two dimensional gas chromatography with fast-quadrupole mass spectrometry detector analysis of polar compounds extracted from the bio-oil from the pyrolysis of sawdust☆

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ABSTRACT

In this paper it is studied the most polar fractions of bio-oil produced by fast pyrolysis of Lignocel BK40-90 (sawdust from forest timber). The biomass was submitted to the pyrolysis in an existing FCC pilot plant that was adapted for this procedure. The equipment consists of a fluidized bed reactor with nitrogen injection. The unit operates with continuous biomass feeding and continuous solids circulation. The produced bio-oil was submitted to an aqueous alkaline extraction, isolating the acidic compounds that were analyzed by one-dimensional gas chromatography and comprehensive two-dimensional gas chromatography with quadrupole mass spectrometry detection (qMS). One hundred and thirty compounds (mainly phenols and ketones) were tentatively identified in the extract, some of them by the use of retention indexes. The main differences between chromatographic techniques were the substantial increasing in the peak capacity of GC × GC and the resolution of some co-elutions that occurred in GC/qMS. It is also possible to conclude that this extract is rich in important raw materials for the chemical industry and can be used for this end.

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1. Introduction

The biomass can be characterized as any resources that can be used for energy production [1], covering a range of materials such as organic wastes, forestry and agriculture residues and can be used in the production of biofuels and also as starting material for chemical and food industries [1,2] with no environmental impact [3,4].

Pyrolysis of biomass can transform it in a product with higher added value (bio-oil) [4] which is produced by the depolymerization and fragmentation of the three major components of biomass: cellulose, hemicellulose and lignin [5] and comprising molecules of different sizes, according to the type of biomass and pyrolysis process employed [6].

The use of bio-oil in the manufacturing industry includes many possible applications such as fuel systems for heat or energy generation [7] and also for transport, after up-grading process [8]. One problem in the use of bio-oil as fuel, is the presence of phenols and the extraction of these phenols can be considered a kind of "up-grading" process [9]. On the other hand, the extracted phenols can be used as raw material for chemical industries. From the bio-oil it was also possible to recovery an hydro-sugars such as levoglucosan, and other compounds that can be used for producing pharmaceuticals, surfactants, biodegradable polymers, resins and fertilizers [10–13].

Many publications involving one-dimensional gas chromatographic analysis(GC/MS) have been reported, with the most varied types of bio-oils [4,6,14–19]. Due to the high molecular complexity of these samples, comprehensive two-dimensional gas chromatography(GC × GC), becomes a more efficient alternative to its characterization due to its high sensitivity, resolution and efficiency [4,6,20].

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Currently, with the development of a system of fast quadrupole mass spectrometry, allowing high acquisition rates, with values up to 50 Hz, it was consolidated the application of this more robust and less costly detector (if compared to TOFMS—time-of-flying mass spectrometry) in the GC × GC for the analysis of complex samples [21].

An important tool that assists the identification of the compounds is the Retention Index (RI), which was first studied isothermally by Kovats [22] and subsequently with Linear Temperature Programmation (LTPRI) by van den Dool and Kratz [23,24].

Then the aim of this paper is the application of the of the GC × GC/qMS technique and the LTPRI system for the analysis of the “up-grading” fraction of a bio-oil generated from the pyrolysis of sawdust, with the goal to characterize the phenols in this sample.

2. Experimental

2.1. Samples and materials

The sample of bio-oil was provided by the company PETROBRAS company and obtained through the process of fast pyrolysis of Lignocel BK40-90 (sawdust from forest timber) supplied by the J. Rettenmaier & Söhne GMBH + CO. The biomass was submitted to the pyrolysis in an existing FCC pilot plant, described in details in a previous paper [3]. The equipment consists of a fluidized bed reactor with nitrogen injection. The reactor is connected to a supply biomass system, which comprises an agitated hopper and a screw conveyor. Another vessel, a fluid bed regenerator, allows the burning of coal and coke produced by the pyrolysis reactions. The unit operates with continuous biomass feeding and continuous solids circulation.

The biomass was used in a particle size range between 300 μm and 500 μm and its weight composition was: moisture = 7.4%; C = 46.1%, H = 6.3%, N = 0.3%, O = 46.7% (calculated by difference) and ash = 0.6% [3].

This crude bio-oil (without any pre-treatment) was the subject of a previous work [3]. All solvents (dichloromethane, hexane, chloroform) and the reference standards (linear alkanes) used were of chromatographic grade (JT Baker, Phillipsburg, NJ, USA, and Sigma Aldrich, Saint. Louis, MO, USA). Other reagents (sodium hydroxide, hydrochloric acid and anhydrous sodium sulfate) were p.a. grade and purchased from Merck (Darnstadt, Germany).

2.2. Liquid–liquid extraction (LLE) procedure

With the aim of isolating the phenols (the expected major compounds in this sample), the bio-oil was subjected to a liquid–liquid extraction based on the work developed by Almeida et al. [25]. The bio-oil was extracted with two portions of 10 mL of aqueous sodium hydroxide (0.1 mol L^{-1}) and washed with three portions of 5 mL of distilled water generating two phases: one aqueous (AP) and other organic (OP). The aqueous fraction was acidified with aqueous HCl solution (1 mol L^{-1}) until pH 2. The aqueous fraction was sequentially extracted with 5 mL of hexane (3 times), 5 mL of dichloromethane (3 times) and finally with 5 mL of chloroform generating three extracts (one for each solvent).

The extracts were combined and washed with three portions of 5 mL of bi-distilled water. Anhydrous sodium sulfate (previously dried in an oven at 200 °C for 12 h) was added to the flask containing the extracted organic phase to remove any residual water. This extract was filtered and the solvents evaporated, being called AAE (Alkaline Aqueous Extract). The extraction was performed in quintuplicate.

2.2.1. Mass yield (%)

After the evaporation of solvents, each fraction (AAE and OP) was suitably weighed to obtain the mass yield expressed in w/w % (weight/weight %).

Solutions at 5000 mg L^{-1} for the sample, in dichloromethane, were used for the chromatographic analysis.

2.3. GC/qMS

The sample and standards were analyzed by GC/qMS (Shimadzu QP2010 Ultra, Shimadzu, Tokyo, Japan) equipped with an AOC20 autoinjector (split/splitless). The chromatographic separation was performed on a capillary column DB-5 (methyl silicone with 5% of phenyl group—60 m in length × 0.25 mm i.d. × 0.25 μm film thickness). The oven temperature was programmed as follows: 40 °C, heating at 3 °C min^{-1} to 120 °C, heating at 2 °C min^{-1}until 200 °C and then heating at 10 °C min^{-1}until 280 °C and stayed at this temperature for 5 min.

The injector, ion source and interface temperature used was 250 °C, the injection was done in the split mode 1:20 and the carrier gas flow rate (He, ultra pure, Linde Gases, Porto Alegre, RS, Brazil) was 0.91 mL min^{-1}. The mass spectrometric conditions were: energy of 0.82 kV and mass scan range from 35 to 400 Da, corresponding to a frequency of 52 Hz. This frequency of acquisition is higher than the normal quadrupole instruments and allows obtaining more than five modulations per peak. All data were treated by the GCMS solution software 2.6.1 (Shimadzu, Japan), using a signal/noise equal to 3. The compounds were tentatively identified using the spectral library database NIST-05. The identification uses the spectra comparison (with the libraries—NIST and WILEY) and also the detailed analysis of MS spectra and the position (retention time) in the chromatogram. It was considered tentatively identified only the peaks where the similarity with the libraries was higher than 80%.

2.4. GC × GC/qMS

The same sample was analyzed by GC × GC/qMS (Shimadzu QP2010 *Ultra* Shimadzu, Tokyo, Japan) equipped with a modulator ZX1-GC × GC (Zoex, Houston, TX, USA). This modulator utilizes liquid nitrogen (Linde Gases, Porto Alegre, RS) for the cold jet (which is continuous) and gaseous nitrogen for the hot jet (activated only for a short period of time).

The chromatographic separation in the first dimension was performed in the same column used in GC/qMS. In the second dimension it was used a more polar column DB-17, 50% phenyl and 50% methyl-polysiloxane (2.15 m × 0.18 mm × 0.18 μm, J&W Scientific, Agilent Technologies, USA). The temperatures of injector, interface, ion source and oven were the same of GC/qMS. The injection was performed in the split mode 1:20 and helium (ultrapure, Linde Gases, Porto Alegre, RS, Brazil) was used as a carrier gas at a flow rate of 0.91 mL min^{-1}. The conditions of the mass spectrometry detector were also the same used in the one dimensional analysis. It was used a modulation period (MP) of 4 s and the time of hot jet was 0.8 s (time in which the hot jet is turned on). The processing of data obtained by GC × GC/qMS was done by the software GC Image 2.2b1 (ZOEX Corporation, Houston, Texas, USA) and for the identification of compounds it was used the NIST-05 library with similarity of at least 80% and confirmation through LTPRI.

2.5. LTPRI

A standard mixture of *n*-alkanes (C6-C30) was injected (1 μL) in the GC × GC/qMS system under the same conditions used for the samples. There tention indices were calculated for each compound in the sample and the values were compared to literature values

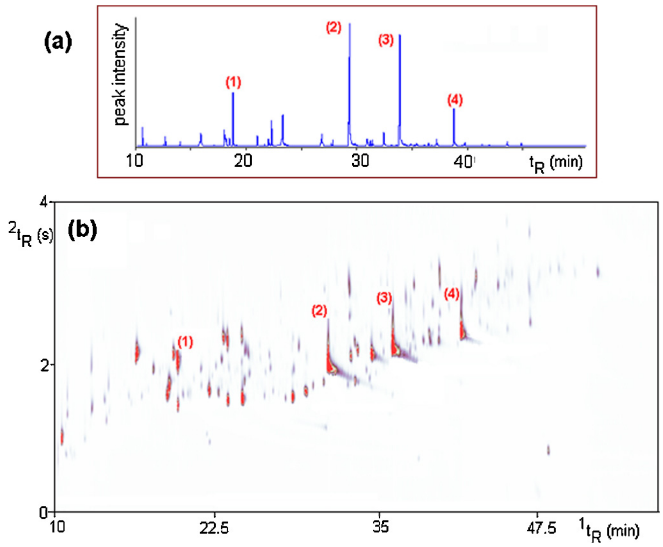

Fig. 1. Chromatograms of the alkaline aqueous extract from bio-oil: (a) GC/qMS and (b) GC × GC/qMS. Major compounds highlighted: (1) phenol, (2) 1,2-benzenediol, (3) 4-methyl-1,2-benzenediol, (4) C2-benzenediol. Chromatographic conditions described in Section 2.

for the same column (DB-5). The data base used in this work was the NIST library [26], and for the LTPRI analysis, it was considered the sum of the retention times of the first and second dimension [27].

3. Results and discussion

It was obtained a mass yield of 4.7% (STD = 1.5% for five successive extractions) for the alkaline extraction from the bio-oil. It is expected that mainly phenolic compounds compose this fraction. As the procedure was done in quintuplicate, all the extracts were mixed to form only one sample.

Fig. 1 shows the chromatographic profiles of the extract (GC/qMS and GC × GC/qMS). In Fig. 1(a) it is shown the one-dimensional chromatogram (GC/qMS)with the major compounds (1, 2, 3 and 4) highlighted. They were identified as: (A) phenol (t_R = 18.82 min, area % ≅ 8.2%), (B) 1,2-benzenediol (t_R = 29.39 min, area % ≅ 21.6%); (C) 4-methyl-1,2-benzenediol (t_R = 33.96 min, area % ≅ 22.4%); and (D) C2-benzenediol (t_R = 38.78 min, area % ≅ 7.5%), respectively.

Thirty five compounds were tentatively identified by GC/qMS (being twenty also confirmed by LTPRI) in this fraction and they belonged to the classes of aldehydes, ketones, ethers, phenols and acids (Table S1 in Supplementary electronic material). Regarding the number of compounds, phenols and ketones represent around 80% of the total of identified peaks, while in terms of area these classes correspond to more than 93% of the total. Considering only the benzenediols, they represent more than 55% of the sample. The concentration of 4-methyl-1,2-benzenedioland 1,2-benzenediol are markedly superior to the other compounds, representing more than40% of the total identified.

Fig. 1(b) shows the color diagram by GC × GC/qMS for the extract, also highlighting the major compounds (that are the same found in the GC/qMS). By this analysis, 130 compounds were identified (phenols, ethers, ketones, aldehydes, acids, alcohols and aromatic hydrocarbons). From these, 57 compounds were confirmed by LTPRI, corresponding to 43.8% of the total identified (Table S2 in Supplementary electronic material).

The relative concentration (only semi-quantitative) is expressed in this work as vol% (volume of the tridimensional peak of each compound divided by the total volume of peaks × 100), and the major compounds were 4 methyl 1,2-benzenediol (12.1%); 1,2-benzenediol (11.1%); C2-benzenediol (7.1%); phenol (4.8%), as can be seen in Fig. 2. This figure shows the distribution of the major compounds using both techniques. The class of phenols has more than 60% of the total volume and, together with the ketones, represents more than 85% of the sample.

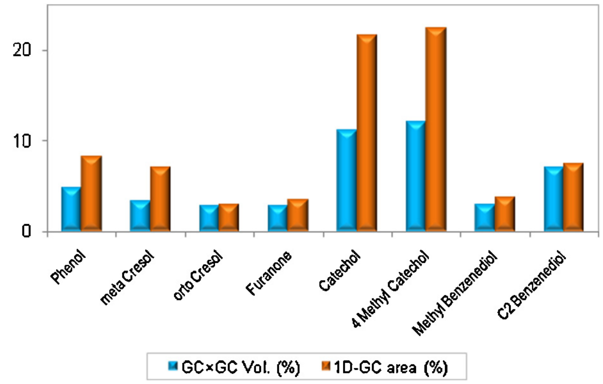

Fig. 2. Distribution o f the major compounds in the sample using both techniques: GC/qMS and GC × GC/qMS.

Regarding the number of compounds, phenols (48 compounds) and ketones (49 compounds) were also the majority classes, representing together more than 74% of the sample. The comparison of the class distribution according both techniques can be viewed in Fig. 3. Only the benzenediols represent more than 40% (by peak volume) of the sample, thus being largely responsible by its high concentration of phenols. This concentration of phenols in this sample indicates that the extraction technique was quite selective.

For better detailing the characterization of each main class of compounds, it was constructed the Dispersion Graphics (using software Excel^{TM}) that can be viewed in Fig. 4. These graphics were constructed using the retention times that were plotted (first dimension *versus* second dimension) for each identified peak, allowing a better visualization of the spatial classification of each compound class. This figure shows the classes of phenols, ketones and acids. In Fig. 4(a) one can observe the spatial distribution of all the chemical classes in the sample. This figure has the same information of Fig. 1(b) but is more qualitatively informative because all the peaks are transformed in points with the same intensity (independent of the concentration). As can be seen, phenols and ketones (points in red and green) are majority and show a certain spatial correlation, for this reason they are also presented in separated figures (Fig. 4(b) and (c)). Fig. 4(b) shows the distribution of alkyl phenols and alkyl benzenediols in detail, while Fig. 4(c) shows the distribution of the cyclic ketones.

As can be observed in these figures, the phenols (with one or two hydroxyl groups) are distributed according to their molecular weight and the number of carbons in the side chain.

Benzenediols are more polar than phenols and appear at higher retention time in the second dimension. Their spatial structuration is not as clear as in the case of mono-hydroxylated phenols due the higher number of isomers (catechol, resorcinol and hydroquinone and their alkylated homologues). It is possible to see also that many co-elutions were resolved in the second dimension. The number of alkyl-phenols increased from 10 to 25 while the number of peaks of the alkyl-benzenediols grew from 6 to 16 (see Tables S1 and S2, in Supplementary electronic material).

In the case of ketones, it is shown the distribution of cyclic ketones, common derivatives of cellulose and hemicelluloses, and it is highlighted the similar behavior of furanones and cyclopentenones and also for pyranones and cyclohexenones. They occupy nearby regions on the two dimensional chromatographic space.

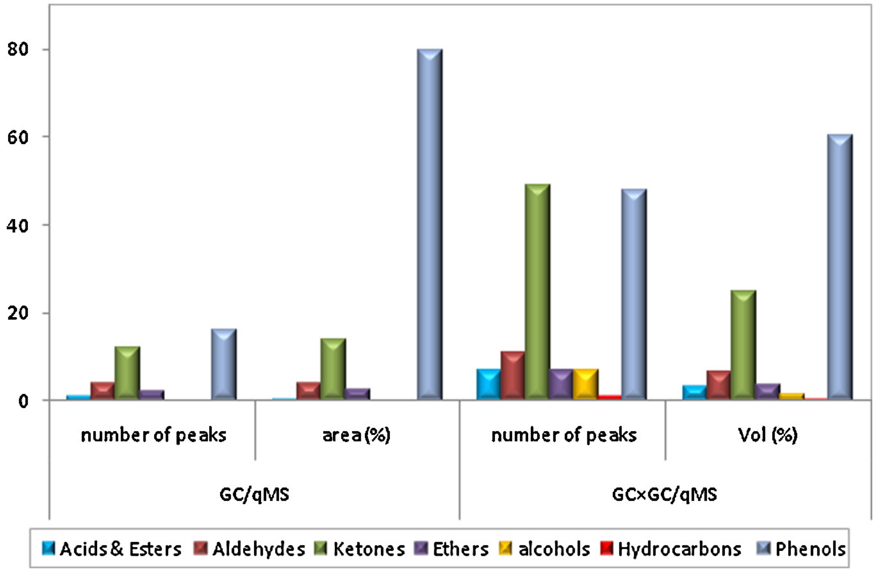

Fig. 3. Summary of the data in terms of number of peaks and semi-quantitative analysis, for each technique (1D-GC and 2D-GC) for the analysis of the sample.

This distribution can be also used to confirm the identification of each compound.

This classification is not so clear for the other classes of compounds due to the less number of isomers, which does not allow the visualization of spatial organization.

Many of the compounds identified in this sample have important industrial uses and reinforce their potential use as chemical inputs. The benzenediols such as hydroquinone and catechol, have many applications as antioxidants and antivirus, inhibitor of vinyl polymerization reactions, antioxidant in the production of rubbers and also in topical application in skin whitening [28–30]. Guaiacol can be used as an indicator in several experiments involving enzymes, due to its feature of changing color, besides being applied in medicine as an expectorant, anesthetic and antiseptic [31]. The presence of ketones as one of the major classes in the sample demonstrates the possibility of application in chemical syntheses. Some compounds such furanones, have application as precursors in the synthesis of brominated derivative fungicidal coatings, and are currently obtained only by extraction of marine algae [31–33].

It is also interesting to note that phenols and ketones are found in another bio-oils from pyrolysis of different biomasses [4,6,10,13–19,27,34–36] but this is the first study of aqueous phase of pyrolysis using GC × GC. In another work developed recently [37] the aqueous phase of a bio-oil from oak was analyzed by LC × LC and the authors also found a great amount of phenols.

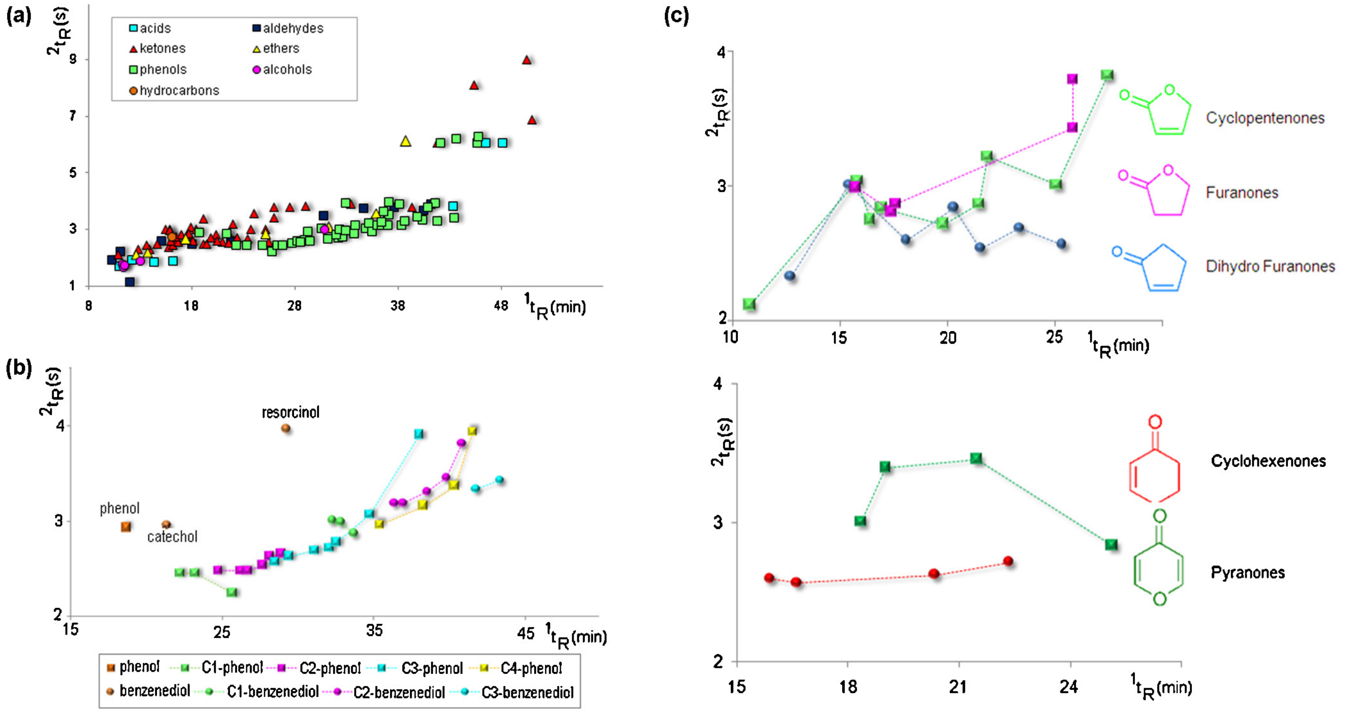

Fig. 4. Dispersion graphics for the compound classes on the alkaline aqueous extract of the bio-oil: (a) total sample; (b) phenols and (c) ketones.

4. Conclusions

The analysis by GC × GC/qMS, associated to the use of LTPRI allowed a qualitative and semi-quantitative characterization of the aqueous alkaline extract from the bio-oil of the pyrolysis of lignocel (sawdust). The extraction procedure of the more polar compounds from the bio-oil, mainly ketones and phenols, is very simple and can be used as a way of "up-grading" of the bio-oil. Many phenols, ketones, acid, aldehydes and ethers with interesting industrial applications were identified in the extract, which can also indicate that this material can be recovered from the bio-oil for using as raw material for many kinds of synthetic procedures, adding value to this material. The two dimensional chromatographic system, coupled to a quick-scan quadrupole mass spectrometer represents a great impulse in the two-dimensional analysis, because this detector is robust, simple, reproductive, sensitive and cheaper if compared to time-of-flight mass spectrometer detector, that is the most used for complex samples.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2014.06.053.

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